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A STUDY OF TUNGSTEN-TECHNETIUM ALLOYS

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by

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A STUDY OF TUNGSTEN-TECHNETIUM ALLOYS

Technetium is a sister element to rhenium and has many properties that are similar to rhenium. It is predicted that technetium will have about the same effects on tungsten as rhenium in regard to increase in workability, lowered ductile to brittle transition temperature, and improved ductility.

The objectives of the current work are to recover technetium from fission product wastes at Hanford Atomic Products Operation and reduce to purified metal; prepare W-Tc alloys containing up to 50 a/o Tc; fabricate the alloy ingots to sheet stock, assessing the effect of technetium on workability; and perform metallurgical and mechanical property evaluation of the fabricated alloys.

Eight hundred grams of technetium metal has been prepared from fission product Tc-99 isolated from 23,000 gallons of Purex plant wastes. The initial separation and concentration was performed by the Chemical Processing Department and is not part of the present program; however, a brief description of this operation is included in this report.

The isolation of the technetium was carried out in four stages which includes two anion exchange cycles followed by preparation of pure ammonium pertechnetate and reduction of ammonium pertechnetate to metal in a hydrogen furnace. Each of these steps is summarized in this report.

Separation from Purex Waste

A total of 23,000 gallons of the supernate from Purex neutralized waste was passed through a bed containing 50 cubic feet of IRA-401 resin in the nitrate form. The technetium which was absorbed on the resin was eluted with ~ 600 gallons of 6.0M nitric acid. This was concentrated to a volume of 100 liters by boiling. Water was added to hold the nitric acid concentration below 10M to prevent loss of technetium by volatization. The

product was transferred to Hanford Laboratories for final purification. The product was analyzed and found to contain the following:

Volume - 100 liters

Fe	49	g/l
Ni	7.5	g/l
Cs	~10	g/l
H^+	2.1	g/l
NO_3^-	337	g/l
Tc	9.80	g/l
Ce-144	273	mc/liter
Ru-106	13	mc/liter
Cs-137	15	mc/liter
Zr-Nb-95	400	mc/liter

Second Cycle Anion Exchange Purification

The iron, chromium, nickel and radioactive contaminants in the technetium supplied by the Chemical Processing Department made a second cycle ion exchange purification step necessary. The relatively high radiation dose rate from Zr-Nb-95 was reduced by a factor of 20 by passing the solution through a lead shielded bed of silica gel. Further operations could then be done in unshielded facilities.

The feed solution pH was adjusted to 1.0 by addition of 16.5 liters of 19M sodium hydroxide. At this pH a small amount of solids were formed. This adjusted feed was passed through a 23 liter bed of IRA-401 resin in the nitrate form. The resin bed was backwashed with 120 liters of 0.05M nitric acid to remove the solids which had collected on the resin and was then washed in the forward direction with an additional 120 liters. The technetium was then eluted with 134 liters of 8.0M nitric acid and collected in eight fractions. The process proceeded smoothly with the exception of gas formation during the elution cycle. It was necessary to degass occasionally to alleviate excessive pressure drop across the bed.

No technetium breakthrough occurred during the loading step. The backwash removed 40 grams Tc which has been saved for future recovery. The

loading and wash effluent contained 10 g. Tc. The product contained 932 g. Tc for a recovery of 94%. Decontamination factors for radioactive contaminants were:

Ce	2×10^3
Ru-106	10
Cs-137	$>> 10^3$
Zr-Nb-95	3×10^3

The nitric acid in the product was destroyed by reaction with formaldehyde and the solution was concentrated 4.5 liters (~200 g/l Tc). The final nitric acid concentration was 2.0M. Losses of Tc during concentration were negligible.

The product of the denitration step was filtered through a medium porosity glass filter to remove traces of solids.

Preparation of Ammonium Pertechnetate

The technetium was converted to ammonium pertechnetate, NH_4TcO_4, in 5 batches by adding concentrated NH_4OH to give a concentration of 3.6M NH_4^+ and 1.0M H^+, cooling to 4 C and filtering the crystals on a medium porosity glass filter. The crystals were washed with five 100-ml portions of 2M NH_4NO_3 - 0.5M HNO_3 followed by two 100-ml portions of 5M NH_4OH and finally with three 100-ml portions of distilled water. The material was dried at 80 C at a pressure of 8 inches of mercury and was ground to a powder. A total of 1560 g. NH_4TcO_4 was recovered. About 80 grams of Tc in the supernate and washes has been retained for further processing.

Analysis of the ammonium pertechnetate show the following impurities, all of which are present at much less than 50 ppm:

Al, Fe, Mg, Mn, Ni, Pt, and Si

Reduction of NH_4TcO_4 to Tc Metal

The reduction to metal was accomplished by reduction in two stages in a hydrogen furnace. The furnace used was a 2-inch x 18-inch tube type. A

Vycor tube and Vycor boats were used. Batch sizes were 200 grams NH_4TcO_4.

Air was expelled from the tube by flushing with argon. The NH_4TcO_4 was then heated to 200 C in H_2 and held at that temperature until the reaction forming TcO_2 was complete. This reaction was quite vigorous and exothermic. Small losses (~ 1%) of technetium by volatilization were incurred at this point. Most of the volatilized technetium was retained in a water scrubber and will be recovered.

The temperature was then increased to 800 C in 50° increments and held for 2 hours. The conversion to metal appears to start at 350 C and is essentially complete in 45 minutes.

A total of 800 grams of metal has been made. Analysis of the oxygen content has not yet been completed.